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ABSTRACT

The fabrication of cylindrical briquettes from Carol Lake iron ore concentrates by vacuum extrusion using polymers and calcium carbonate as plasticizer and binder is described. The strength of the indurated products made from the crude iron ore concentrate is below the ISO specification. However, if the ore is roasted at 750 to 850°C to convert the magnetite in the ore to hematite, a substantial improvement in strength (2 to 4 times) in the indurated briquettes occurs which makes them even stronger than the requirement.

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EXTRUSION ET DURCISSEMENT DU MINERAI DE FER PROVENANT DE CAROL LAKE EN UTILISANT DES POLYMÈRES ET DU CARBONATE DE SODIUM COMME LIANTS

A.K. Kuriakose* et D.H.H. Quon*

RÉSUMÉ

La fabrication de briquettes cylindriques par extraction sous vide de concentrés de minerai de fer en provenance de Cold Lake en utilisant des polymères et du carbonate de calcium comme plastifiants et liants est décrite dans ce rapport. La résistance des produits durcis fabriqués à partir du concentré brut de minerai de fer ne répond pas aux normes de l'ISO. Cependant, si le minerai de fer est grillé à une température de 750 à 850°C afin de transformer la magnétite qu'il contient en hématite, une amélioration considérable (de 2 à 4 fois) de la résistance des briquettes durcies s'ensuit les rendant plus résistantes que ne l'exige les spécifications de l'ISO.

INTRODUCTION

In North America, iron ore feed for blast furnaces is produced by pelletizing iron ore fines. This is achieved using 0.3 to 1.0 wt % of bentonite and the required amount of water for balling in a disc or drum pelletizer. Bentonite has been the major binder in the pelletization process for decades. However, the presence of bentonite in the pellets has a detrimintal effect on steel production, as it introduces silica, alumina and alkali into the system. Also, the supply of high grade bentonite necessary for the process is becoming depleted. Hence there is a need to develop alternative bonding agents which can be substituted for the bentonite in the pelleting process.

In an earlier report (1) a method has been described by which pellets are fabricated from hematite concentrates by cold extrusion using organic polymers and calcium carbonate as plasticizer and binder. These pellets exhibited satisfactory green and dry crushing strength. Actually, the indurated pellets developed a crushing strength significantly higher than that of the pellets containing bentonite. In the present study, the extrudability of the iron ore concentrates containing both magnetite and hematite with organic polymer and calcium carbonate and the physical characteristics of the resulting extrudates are examined and reported.

EXPERIMENTAL PROCEDURE

RAW MATERIALS

Iron Ore Concentrate from Carol Lake

This consists of mainly hematite and appreciable amounts of magnetite with small amounts of quartz and feldspar, as determined by X-ray diffraction. The fine concentrate was used as received, and also after calcining in air at 750°C which converted most of the magnetite in the ore into hematite.

Binders

The organic binders selected were carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxyethyl cellulose (HEC) and alginate, as in the earlier work (1). The inorganic additive for high temperature strength was also the same i.e. calcium carbonate.

Prior to the pellet extrusion, the plasticity of the iron ore with the binder system was determined using a Brabender plastograph (2). The procedure for the plasticity determination has been described elsewhere (3).

The mixtures for extrusion were prepared by combining appropriate amounts of the constituents with the required amount of water (as determined from the plasticity measurement results) in a blender until a uniform dispersion of the components was obtained. An auger type extruder was used to produce pellet batches of about 4 kg; a vacuum of about 63 cm of Hg was maintained in the extrusion chamber. The die was designed to simultaneously extrude three columns, each having a diameter of about 2.5 cm. A metal wire device was used to cut cylindrical pellets of desired length as soon as the extrudate emerged from the die.

The strength of the green pellets was determined by a drop test and the dry crushing strength was measured after drying them in an oven at 120°C for 24 h. Some of the oven-dried pellets were heat-treated at various induration temperatures ranging from 500 to 1300°C for periods of 10 to 20 minutes. Usually, the furnace was preheated to the required temperature and a quantity of the dry pellets (placed in an alumina container) was pushed into the hot zone; the time of heating of the pellets from room temperature to the test temperature was normally less than 10 minutes. On completion of the induration cycle, the pellets were cooled and tested for crushing strength.

The reaction of the binders and iron ore at various temperatures was determined using differential thermal analysis (DTA).

RESULTS AND DISCUSSION

PLASTICITY OF THE IRON ORE WITH THE ORGANIC AND INORGANIC BINDERS

The plasticity development of the iron ore concentrate with varying amounts of organic and inorganic binders is plotted in Fig. 1, and the peak plasticity values are recorded in Table 1. The results indicate that a greater consistency of the mixture is developed in the sample containing MC than in the others. The water contents corresponding to the peaks are only slightly different (10 to 11.8 wt %) for the various binders.

EXTRUSION OF MIXTURES AND THE DRY STRENGTH OF THE PELLETS

Iron ore concentrate compositions containing 0.25 and 0.5 wt % of MC, CMC, HEC or alginate and 1 to 2 wt. % $CaCO^3$, based on the results of the plastograph experiments, were extruded, and cylindrical specimens of about 2.5 x 2.5 cm in size were produced. For comparison, extrudates containing bentonite, calcium carbonate and organic binder were also prepared. The green pellets were oven-dried at 120°C and their crushing strength was determined. Dry strength of the pellets containing different binders is given in Table II. The extrudates containing alginate and CMC show considerably higher strength than those containing HEC, MC and bentonite.

EFFECT OF TEMPERATURE ON THE REACTION OF THE EXTRUDATES

Prior to the induration of the extrudates, DTA was used to examine the reactions of the various binders and iron oxide in the pellets. The resulting curves, shown in Fig. 2 to 4, indicate that the organic binder is oxidized at a temperature below 400°C, as revealed by the exothermic peak at about 240 to 375°C. Another exothermic peak at 680°C is due to the oxidation of the magnetite to hematite. The endothermic peaks at 570, 680°C and 810°C are due to the alpha to beta quartz transformation, Curie temperature of the hematite and decomposition temperature of the calcium carbonate respectively.

STRENGTH DEVELOPMENT OF PELLETS AFTER BINDER BURN-OFF

Based on the DTA curves of the various composition, the organic binders decompose and become oxidized at a temperature well below 850°C. The loss of the organic binder from the pellets would undoubtedly affect the strength of the extrudates. To determine this loss of strength, the extrudates were heated at 850°C for 20 minutes and the strength of the heat-treated pellets measured. The results are given in Table III. As expected, an appreciable strength-loss occurrs as a result of the binder decomposition.

INDURATION AND STRENGTH DEVELOPMENT OF THE EXTRUDATES

The various extruded briquettes were indurated at temperatures of 1050, 1150, 1250 and 1300°C for 10 to 20 min. and the crushing strength of each product measured. These results are presented in Table IV and are discussed in the following section.

Extrudates of Untreated Carol Lake Ore

In this system, a satisfactory crushing strength of over 2000N is shown only by the product made using MC and calcium carbonate as the binders, even after induration at 1300°C for 20 min. However, this is considerably less than the values reported (~5000N after induration at 1300°C) in the case of Mount Wright iron ore concentrate using the same binders (1). The main difference between the two types of iron ore concentrate is that the Mount Wright ore is almost all hematite while the Carol Lake ore is hematite plus a large proportion of magnetite. This difference is clearly visible in the DTA curves for the two types of ores in air when Fig. 5, this report and Fig. 7 in (1) are compared; the Carol Lake ore shows an exothermic peak at about 680°C due to the oxidation of the magnetite, which is absent in the Mount Wright ore. The significant difference in the indurated strength must hence be attributed to the differences in the physical and chemical properties of the two materials, resulting from the compositional differences. To verify this theory, a quantity of the Carol Lake ore was roasted in air at 750 to 850°C and a series of extrusions were made with the resultant concentrate. Results of these experiments are also included in Table IV and Fig. 7. These and other details on the calcined Carol Lake ore are discussed below.

Roasted Carol Lake Ore

A cursory glance through Table IV and Fig. 6 & 7 indicates that the crushing strength of the oxidized Carol Lake ore is significantly higher than that of the uncalcined ore. The strength of the product made from oxidized Carol Lake ore with MC and calcium carbonate after induration at 1300°C is over 8000N as compared to under 3000N for the product made with the uncalcined ore. The strengths of the remaining compositions are also in the acceptable range of over 2000N after induration at 1250 or 1300°C when

the roasted ore is used. The calcination has a significant beneficial effect when bentonite is used as a binder also, the strengths being 3200 and 12066N without and with calcination of the ore (Table IV).

Bentonite-Calcium Carbonate-Organic Binder Mixtures

The strength development of the extrusions containing 0.25% MC, 1% calcium carbonate and 0.2, 0.4 and 0.6% bentonite with the uncalcined Carol Lake ore concentrates are given in Table IV. The effect of induration temperature on the strength indicates that the strength increases with increasing induration temperature beyond 850°C and that this increase in strength is independent of the amount of bentonite added in the range reported when mixed with calcium carbonate and MC. However, the roasted Carol Lake ore shows an almost fold-four increase in strength with the same ingredients as binders.

THE REASONS FOR IMPROVED STRENGTH AFTER CALCINATION OF THE ORE

Although the increase in the strength of the product after induration is related to the oxidation of the magnetite to hematite, the actual mechanism behind the strengthening is not obvious. The particle size of the ore could have changed after roasting; the reactions between the sintering aids and the ore could be different also. To determine the change in particle size in the ore after calcination, the surface areas of the concentrates were determined before and after calcination, by the B.E.T. method using a Quantachrome surface area analyser. The surface area values obtained for the two samples were identical - 0.52 m^2/g, showing that the calcination did not affect the surface area and hence the particle size.

An examination of the phase diagram (4) of the system iron oxides-silica-calcium oxide reveals that the liquid phase formed below about 1300°C consists of calcium ferrites which are compounds produced by the reaction between calcium oxide and ferric oxide (hematite). Calcium oxide and magnetite do not combine readily in this temperature range to form any low melting compounds. The liquid phase formation is very important in the densification and strengthening of the extrudates. This explains the increase in the strength of the extrudates on calcination of the Carol Lake ore in air and also the high strength of the products made using Mount Wright ore. (The latter is almost all hematite).

CONCLUSIONS

Carol Lake concentrate mixed with organic polymers and calcium carbonate can be extruded into products with satisfactory wet and dry strength, but they lack the required high strength after induration. This is in contrast to the results of similar studies with Mount Wright concentrates where satisfactory strengths are obtained both before and after induration. The reason for this difference in behaviour is the significant difference between the chemical composition of the two ores. The Mount Wright ore is almost all hematite (Fe_2O_3) while the Carol Lake ore is a mixture of hematite and considerable amounts of magnetite (Fe_3O_4). During induration, in the case of Mount Wright ore, the reaction between calcium oxide and the abundantly available hematite produces liquid phases consisting of calcium ferrites which aid in the sintering of the extrudates. However, with the Carol Lake ore, the availability of hematite is considerably less, due to the high proportions of magnetite present, resulting in poorer indurated strength development.

If the Carol Lake ore is roasted at temperatures in the order of 750-850°C which converts the magnetite into hematite by oxidation, then the resulting ore can be extruded and indurated to satisfactory high strengths.

ACKNOWLEDGEMENTS

We wish to express our thanks to the Iron Ore Company of Canada for supplying the iron ore for this study. Thanks are also due to G. Lemieux for his assistance in performing the extrusion experiments.

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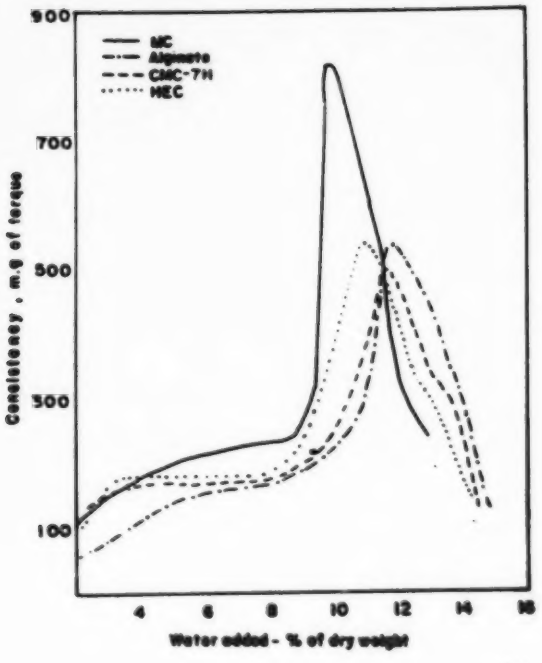

Fig. 1. Consistency of the iron ore concentrate with addition of various polymers

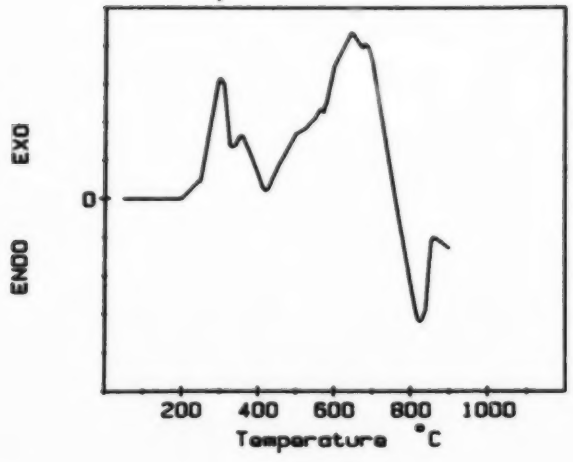

Fig. 2. DTA curve of mixture containing CMC, calcium carbonate and iron ore concentrate in air

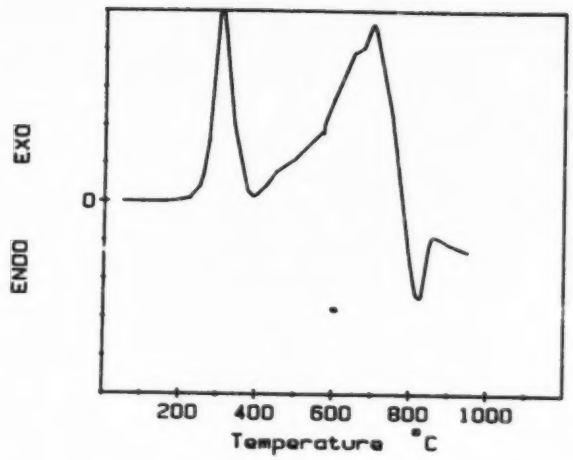

Fig. 3. DTA curve of iron ore containing HEC and calcium carbonate in air

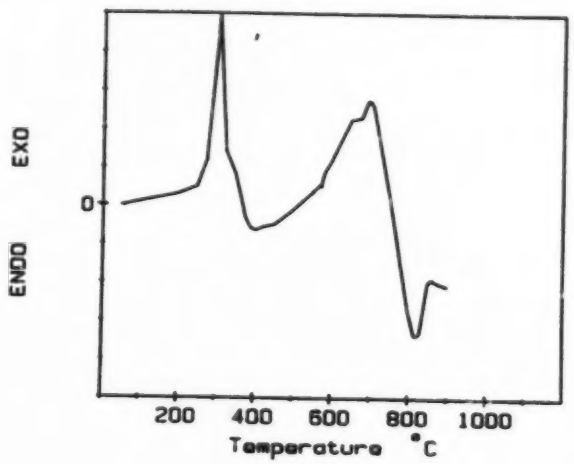

Fig. 4. DTA curve of iron ore containing MC and calcium carbonate in air

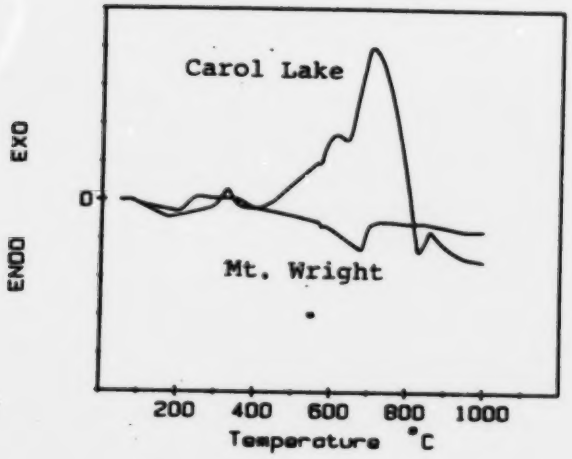

Fig. 5. DTA curves of iron ore concentrate from Carol Lake and Mount Wright in air

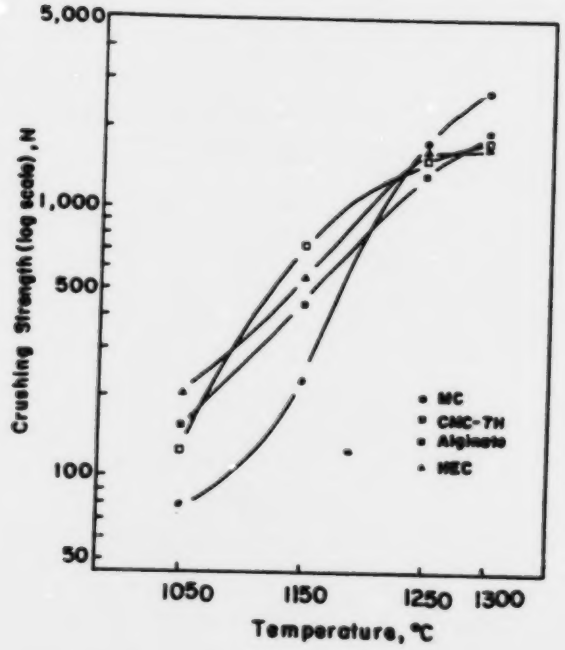

Fig. 6. Strength development of pellets indurated

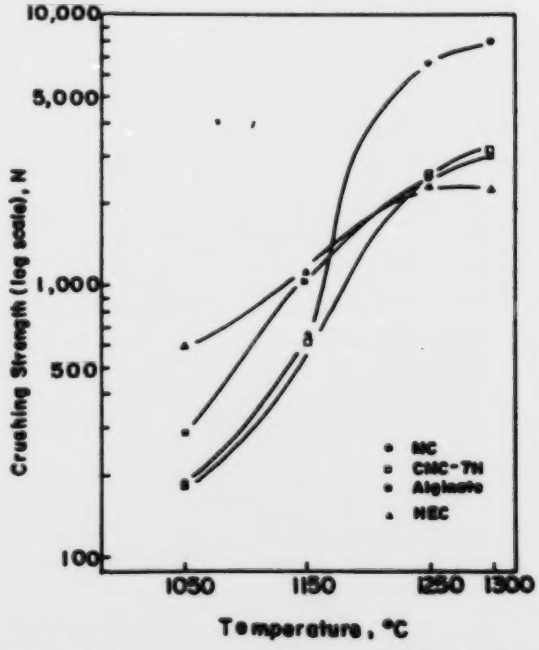

Fig. 7. Strength development of pellets from roasted ore indurated at various temperatures for 20 min.

Table I Peak plasticity values of the iron ore with various additives

	Binder wt %	$CaCO_3$ wt %	water, wt %	peak max.
Na alginate	0.5	1.0	11.0	540
Natrosol 250 (HEC)	0.25	1.0	11.0	540
Methylcell-(MC)(3000)	0.25	1.0	10.0	815
CMC-7H	0.25	2.0	11.5	500

Table II The strength of the various dry extrudates

Binder	Dry pellet strength, N
0.5% Alginate & 1% $CaCO_3$	886
0.25% HEC & 1% $CaCO_3$	366
0.25% MC & 1% $CaCO_3$	383
0.25% CMC-7H & 1% $CaCO_3$	1033
0.2% Bentonite, 0.25%MC & 1% $CaCO_3$	500
0.4% Bentonite & 0.25%MC & 1% $CaCO_3$	480
0.6% Bentonite & 0.25%MC & 1% $CaCO_3$	588

Table IV The strength of extrudates after organic binder burn-off at 850°C

	Strength, N	
	10 min	20 min
0.25% CMC-7H & 1% $CaCO_3$		78
0.25% MC, 0.25 bentonite & 1%$CaCO_3$	39	59
0.25%MC & 1% $CaCO_3$	49	59

Table IV Crushing strength of the pellets indurated at different temperatures and times

			Induration conditions & crushing strength				
Exp. no	Binder	dry strength N	temp C	time m	strength N	time m	strenght N
1	1%CC	886	1300	10	549	20	1947
	0.5% Alginate		1250	10	503	20	1313
	12% water		1150	10	425	20	425
			1050	10	183	20	157
2*	1.0%CC	798	1300	10	1699	20	3112
	0.5% Alginate		1250	10	902	20	2519
	12% water		1150	10	378	20	1027
			1050	10	218	20	289
3	1.0%CC	66	1300	10	908	20	1727
	0.25% HEC		1250	10	287	20	1620
	11% water		1150	10	98	20	715
			1050	10	95	20	124
4*	1.0% CC	472	1300	10	1862	20	3054
	0.25% HEC		1250	10	1463	20	2563
	11% water		1150	10	123	20	654
			1050	10	72	20	186
5	1.0% CC	383	1300	10	425	20	2769
	0.25% MC		1250	10	242	20	1759
	10.5% water		1150	10	72	20	223
			1050	10	59	20	78
6*	1.0% CC	627	1300	10	2083	20	8199
	0.25% MC		1250	10	1470	20	6811
	11% water		1150	10	559	20	625
			1050	10	88	20	186

* Iron ore concentrate calcined at 750 -850°C for 1h.
cc = Calcium carbonate

Table IV Crushing strength of the pellets indurated at different temperatures and times (cont'd)

			Induration conditions & crushing strength				
Exp. no	Binder	dry strength N	temp C	time m	strength N	time m	strenght N
7	2.0% CC	1033	1300	10	588	20	1849
	0.25% CMC-7H		1250	10	526	20	1562
			1150	10	206	20	542
			1050	10	157	20	206
8*	2.0% CC	902	1300	10	2417	20	2448
	0.25% CMC-7H		1250	10	1053	20	2352
			1150	10	441	20	1115
			1050	10	317	20	604
9	0.2% bentonite	500	1300	10	1269	20	3367
	1.0% CC		1250	10	443	20	2516
	0.25% MC		1150	10	132	20	789
	10.5% water		1050	10	68	20	98
10	0.4% bentonite	480	1300	10	1259	20	3094
	1.0% CC		1250	10	422	20	2051
	0.25% MC		1150	10	123	20	666
	10.5% water		1050	10	78	20	121
11	0.6% bentonite	526	1300	10	1335	20	3200
	1.0% CC		1250	10	495	20	2431
	0.25% MC		1150	10	194	20	569
			1050	10	176	20	212
12*	0.6% bentonite	588	1300	10	4246	20	12066
	1.0% CC		1250	10	1839	20	7497
	0.25% MC		1150	10	186	20	1835
			1050	10	93	20	297

* Iron ore concentrates calcined at 750 to 850°C for 1 h.
cc = Calcium Carbonate